

3/PRTS

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# ELECTROLYTE MEMBRANE FOR FUEL CELL AND MANUFACTURING METHOD THEREOF, AND FUEL CELL AND MANUFACTURING METHOD THEREOF

## Technical Field

The present invention generally relates to an ion-selective membrane, and more particularly to an electrolyte membrane for a polymer electrolyte fuel cell.

The present invention also relates to a fuel cell having such electrolyte membrane and a manufacturing method of the electrolyte membrane.

## Background of Invention

The recent encouraged global activities of environmental protection put strong demands for restrictions on greenhouse gases and NOx gas production. In order to reduce the total amount of such exhaust gases, practical application of fuel cell system to automobile is thought to be very useful.

Polymer electrolyte fuel cells (PEFCs) have several advantages: operative at a low temperature; high power density; and generation of water alone during power generating reaction. Among all, PEFCs using methanol as fuel are thought to be a promising power source for an electric automobile since they enables fuel supply in a liquid form like gasoline.

PEFCs are classified into two types: reformed methanol-type polymer electrolyte fuel cells which involve reforming methanol into hydrogen-containing gas using a reformer; and direct methanol polymer fuel cells (DMFCs) which utilize methanol directly without using a reformer. Practical use of direct methanol polymer fuel cells is expected due to their great advantages: weight-saving is possible since direct methanol polymer fuel cells do not require a reformer; resistance against frequent start and stop operations; significantly improved load change response; and substantially reduced catalyst poisoning.

However, several difficulties associated with implementation of DMFC have also been pointed out. For example, DMFCs use a solid-state polymer electrolyte as the electrolyte. However, when a conventional electrolyte membrane for PEFC such as Nafion™ available from Du Pont or Dow membrane available from Dow Chemical is used,

it causes two major problems: methanol will permeate the membrane, and thus the membrane will be directly oxidized and electromotive power will be reduced; and there occurs melting (creeping) of the membrane at an elevated temperature, about 130°C, for increasing catalyst activity. Although no electrolyte membranes exist which can simultaneously resolve these problems, solution of these problems may greatly promote development of DMFC applicable to automatic vehicles.

#### Disclosure of Invention

Accordingly, an object of the present invention is to implement a novel electrolyte membrane that has greatly reduced methanol crossover and is enduring in a high-temperature (about 130°C or higher) environment.

Another object of the present invention is to provide a method for manufacturing the electrolyte membrane.

Further, an object of the present invention is to implement a novel direct methanol polymer fuel cell having the electrolyte membrane.

The present inventors found, after intense studies to solve the above-described problems that a novel electrolyte membrane for fuel cell that can simultaneously resolve these problems may be obtained by filling a polymer having proton conductivity in the pores of a heat-resistant porous substrate, which is substantially swell-resistant against organic solvent and water.

Polymers are generally softened at a higher temperature but they can maintain their properties until they are thermally decomposed. Accordingly, the present inventors assumed that if polymers are embedded into the pores of the heat resistant porous substrate through chemical bond, the framework of the substrate could support the structure of the membrane at elevated temperatures. The novel electrolyte membrane is based on this assumption.

Further, the present inventors invented a novel method for filling the pores of a porous substrate with polymer(s), the process comprising the steps of: activating the surface of the pores of the porous substrate by irradiation with energy such as plasma, UV radiation, electron rays, gamma radiation or the like; and then contacting with or applying to the

activated surface monomers each having an ion exchange group to be allowed to react graft polymerization both on the surface of and in the pores of the substrate, thereby substantially filling the pores of the porous substrate with polymer.

The electrolyte membrane according to the present invention may be characterized by that a polymer having proton conductivity is filled in the pores of a heat-resistant porous substrate having swell-resistance against organic solvent and water.

In the electrolyte membrane according to the present invention, proton conductivity may be provided by the electrolyte embedded in the pores of the porous substrate while the form-stability at higher temperature and swell- and heat-resistances of the membrane may be provided by the porous substrate matrix.

#### Brief Description of Drawings

Figure 1 is a partial cross-sectional view of a porous substrate showing one step of the process for plasma-graft-polymerizing monomers on the porous substrate.

Figure 2 is a partial cross-sectional view of a porous substrate showing another step of the process for plasma-graft-polymerizing monomers on the porous substrate.

Figure 3 is a graph showing the methanol permeation flux for the electrolyte membrane according to the Example (pore-filled membrane) measured by pervaporation and vapor permeation tests, exhibiting the ability of the pore-filled membrane to prevent methanol permeation.

Figure 4 is a schematic view showing one aspect of a methanol fuel cell, which employs the electrolyte membrane according to the present invention.

Figure 5 is a schematic view showing one aspect of a cathode, which employs the electrolyte membrane according to the present invention.

#### Embodiments of the Invention

The present invention will be described hereinafter in more detail.

An electrolyte membrane according to the present invention may comprise, as a substrate, a heat-resistant porous material that does not swell substantially with water and organic solvents such as methanol. Examples of such porous material may be inorganic

materials including glass or ceramics such as alumina and silica; and others including Teflon™ and polyimide. These materials may be used alone, or a composite material made of two or more of the above-mentioned materials. When the substrate comprises the composite material, the substrate may have a structure consisting of two or more layers with each layer consisting of the above-mentioned material.

According to the present invention, percentage of pores may preferably be 10 % to 95 % by volume of the substrate. The average pore size is desirably within the range of 0.001 to 100  $\mu$  m. Thickness of the substrate may be 100  $\mu$  m or less, and preferably in the order of several  $\mu$  m.

In the electrolyte membrane according to the present invention, graft polymer consisting of monomers each having an ion-exchange group is formed at least on the inner surfaces of the pores provided in the porous substrate such that the pores are substantially filled with the graft polymer. Thus, one end of the graft polymer is bound to the inner surface of the pores, which efficiently prevents the graft polymer from flowing or eluting out of the pores easily.

The term "ion-exchange group" herein refers to a group, which carries and easily release proton such as  $-\text{SO}_3^-$  from  $-\text{SO}_3\text{H}$  group. The groups exist in a pendant pattern of the graft polymer, which is then filled in the pores, thereby providing proton conductivity.

Such graft polymerization of monomers may be performed by exciting the substrate with, for example, plasma, UV radiation, electron rays, gamma-radiation or the like to generate reaction start point, and then contacting monomers with the reaction start point. Alternatively, chemical process using silane coupler or the like or any other conventional polymerization process may be used in which polymerization is performed in the pores and then the resultant polymer is bound to the substrate.

According to the present invention, plasma graft polymerization may be most preferably used which will be described below. Plasma graft polymerization may be performed by using the liquid phase process described below and any well-known vapor phase polymerization.

Monomers which can be used in the present invention preferably include, but are not limited to, sodium acryl sulfonate (SAS), sodium methallyl sulfonate (SMS), sodium

p-styrene sulfonate (SSS) and acrylic acid (AA). Also included are monomers which have vinyl groups and strong acid groups such as sulfonic acid or phosphonic acid group, weak acid groups such as carboxyl group, strong base groups such as primary, secondary, tertiary and quaternary amines, or weak base groups, as well as derivatives (e.g., esters) thereof. The Examples of the monomers may include, but being not limited to, allylamine, allyl sulfonate, allyl phosphonate, methallyl sulfonate, methallyl phosphonate, vinyl sulfonate, vinyl phosphonate, styrene sulfonate, styrene phosphonate, sulfonate or phosphonate derivatives of acrylamide, ethyleneimine, methacrylate and the like.

Only one of the above-described monomers may be used to form homopolymer. Alternatively, two or more of the above-described monomers may be used to form copolymer.

Proton conductivity of the electrolyte membrane may depend on the type of monomers to be used. Desirably, material(s) having higher proton conductivity may be used.

Proton conductivity of the electrolyte may also depend on the degree of polymerization of the graft polymer filled in the pores. The degree of polymerization of the graft polymer filled in the pores may be represented by the density of the polymer in the pores. According to the present invention, the graft polymer may have the same density in the pores as the highest density of the polymer obtained under conventional conditions. The density of the graft polymer according to the present invention may depend on the type of the monomer(s) to be used. If the highest density of the polymer obtained under conventional conditions is normalized as 1, the density of the graft polymer according to the present invention may be, for example, 1.2 or less and 0.2 or more represented by the normalized density, in order to have proton conductivity and desired methanol permeability.

Plasma graft polymerization which can be used in production of the electrolyte membrane according to the present invention may involve irradiating a substrate with plasma to generate reaction start point on the surface of the substrate as well as on the inner surface of the pores in the substrate, and then preferably contacting monomers with the substrate by well-known liquid phase polymerization to graft-polymerize the monomers both on the surface and in the pores of the substrate.

Hereinafter, plasma graft polymerization which can be used in the present invention will be described in detail in reference to the drawings. Detailed descriptions regarding plasma graft polymerization are described in the precedent patent applications filed by the present inventors, Japanese Patent Application Laid-Open Nos. 3-98632, 4-334531, 5-31343, 5-237352, and 6-246141.

Figure 1 is a partial cross-sectional perspective view showing a porous substrate 1 which can be used in the electrolyte membrane according to the present invention. The porous substrate 1 has a number of pores 2 provided therein which extend through the substrate from one side to another side.

The porous substrate 1 is plasma-treated in the presence of gas such as argon, nitrogen or air under a pressure in the range of from 1 mPa to 120 kPa, at normal frequency of 10 to 50 MHz, at power of 1 to 1000 W for 1 to 1000 seconds. Then, reaction start point (not shown) may be formed on the surface of the substrate 1 in the region that has been exposed to the plasma (including the inner surface of the pores).

Next, monomer(s) having an ion-exchange group may be dissolved in water to prepare homogenous solution of monomer. Concentration of monomer aqueous solution is preferably within the range of 0.1 to 80 percent by weight.

The plasma-treated substrate 1 is then subject to contact with the monomer aqueous solution. More particularly, the porous substrate 1 having the reaction start point formed thereon may be immersed in the aqueous solution of monomer. This step may preferably be performed at 20 to 100°C while bubbling with inert gas such as nitrogen gas. The substrate 1 may be immersed in the solution for approximately from 1 minute to 1 day.

Then, the porous substrate 1 is removed from the aqueous solution after a predetermined time, washed with organic solvent such as toluene or xylene, and dried. In this way, by-product(s) produced during the polymerization process such as homopolymer can be completely removed by washing with such organic solvent while the graft polymer may be left only on the surface and inner space of the pores in the substrate.

Figure 2 is a perspective view conceptually showing the substrate 1 on which monomer(s) are graft polymerized. It can be seen that the graft-polymerized polymer 3 is formed not only on the surface of the substrate but also in the pores 2 of the substrate such

that the pores are substantially filled with the polymer.

By the above-described plasma-graft-polymerization, an electrolyte membrane can be produced such that pores 2 of a porous substrate 1 are substantially filled with a graft polymer. Since graft polymer according to the present invention is chemically bound to the surface of the substrate, the structure of the membrane may be supported by the substrate 1. Thus, the polymer may not be easily released from the pores 2, and the structure of the membrane is stable even at elevated temperatures unless the polymer is thermally decomposed.

The electrolyte membrane according to the present invention may preferably be used in fuel cells, and particularly in methanol fuel cells including direct methanol polymer fuel cells and reformed methanol-type PEFCs. Most preferably, the electrolyte membrane according to the present invention may be used in direct methanol polymer fuel cells.

Configuration of a methanol fuel cell will be briefly described in reference to Figure 4.

Figure 4 is a schematic view showing one aspect of a methanol fuel cell using the electrolyte membrane according to the present invention.

A methanol fuel cell 11 comprises a cathode 13, an anode 15 and an electrolyte 17 sandwiched therebetween. Alternatively, a reformed methanol-type PEFC may additionally comprise a reformer (not shown) provided on the anode side.

Any conventionally known cathode may be used as the cathode according to the present invention. The cathode may include a catalyst layer and a support layer, for example, wherein the catalyst layer is formed adjacent to the electrolyte and a support layer for supporting the catalyst layer is formed adjacent to the catalyst layer.

Alternatively, any conventionally known anode may also be used as the anode according to the present invention. The anode may include a catalyst layer and a support layer, for example, wherein the catalyst layer is formed adjacent to the electrolyte and a support layer for supporting the catalyst layer is formed adjacent to the catalyst layer.

Further, a methanol fuel cell having an electrolyte according to the present invention may also be obtained by integrating a first electrode together with an electrolyte to form an integrated product, and attaching a second electrode, which is different from the

first electrode, to the product so that the catalyst layer of the second electrode is brought in tight contact with the electrolyte.

A methanol fuel cell having a cathode as the first electrode will be described in reference to Figure 5.

Figure 5 is a schematic view showing one aspect of a cathode having an electrolyte membrane according to the present invention.

As shown in Figure 5, the cathode 13 may comprise a support layer 19 and a catalyst layer 21 formed thereon.

The support layer 19 may be preferably comprised of material which has gas permeability (particularly oxygen gas permeability), heat-resistance and electron conductivity, e.g., porous carbon having electron conductivity.

The catalyst layer 21 carries any conventionally known catalyst suitable for the cathode.

A porous thin layer 23 having a number of pores 2 as shown in Figure 1 may be formed on the catalyst layer 21. Forming processes of the porous thin layer include: preparing a sol that may comprise a variety of silicon alkoxides, aluminum alkoxides, titanium alkoxides or zirconium alkoxides, which will form glasses or ceramics; and then applying the sol to the catalyst layer by any well-known method such as dip coating, spin coating, spray coating or the like. Thus applied sol may be then dried, and if desired heated, to form a porous thin layer. The resultant porous thin layer may be preferably made of silica, alumina (e.g.,  $\gamma$ -alumina), titania or zirconia, or mixture or complex of two or more of these materials.

Pores of the resultant thin porous layer may be then filled with the above-mentioned polymer by, for example, graft-polymerization and preferably by plasma-graft-polymerization such that one end of the polymer is bound to the inner surface of the pores. Thus, cathode and electrolyte may be integrated.

This integrated product may facilitate the handling of the thin electrolyte membrane.

The integrated product may be attached to an anode such that the catalyst layer of the anode is brought into tight contact with the electrolyte of the product.



Although the integration of cathode and electrolyte has been described above, it may be easily contemplated by those skilled in the art that anode may be integrated with electrolyte.

### Example

The present invention will be described in more detail in reference to the following example.

#### Example 1

A porous PTFE membrane was used as the substrate (Teflon™, manufactured by Nitto Denko; plain film; thickness = 70  $\mu$  m; and pore size = 50 nm). The substrate was washed and irradiated with plasma under the following conditions:

Radiofrequency power: 30W;  
Plasma-irradiation time: 60 seconds;  
Atmosphere: Argon gas; and  
Pressure: 10 Pa.

After plasma-irradiation, the substrate was immersed in freeze-deaerated monomer solution for graft polymerization. Conditions used for graft polymerization were as follows:

Monomer: Acrylic acid (AA);  
Monomer concentration: 10 (% by weight);  
Solvent: Water;  
Temperature: About 60°C; and  
Time: 10 to 24 hours.

The porous substrate was removed from the solution, washed in water, and then dried. Next, the dry weight of the membrane was compared to the original weight of the membrane before polymerization, to calculate the graft polymerization weight. The graft polymerization weight was 1.7mg/cm<sup>2</sup>. The resulting membrane obtained by

polymerization had a thickness of about 90  $\mu$  m.

FT-IR (Mapping method) of the resultant membrane was determined to find that the peak of 1740  $\text{cm}^{-1}$  derived from carbonic acid group was also present in the membrane. It shows that the pores in the membrane were filled with polymer.

Figure 3 is a graph showing the ability of the electrolyte membrane (pore-filled membrane) according to this example (AA membrane: polymerization weight = 1.7  $\text{mg}/\text{cm}^2$ ) to prevent methanol permeation measured by two tests: pervaporation test (at 25°C); and vapor permeation test (at 80 to 180°C). For comparison, Nafion™ membrane was also subjected to the same tests. Water/methanol (10/90 percent by weight) was supplied under its equilibrium vapor pressure at 25°C. The abscissa axis of the graph shows temperature (°C) and the vertical axis shows the permeability flux.

As shown in Figure 3, in pervaporation test at 25°C the pore-filled membrane exhibited very low methanol flux of 0.042  $\text{kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ , apparently indicating its better ability to inhibit methanol permeation when compared to that of Nafion membrane at the same temperature.

Further, vapor permeation test showed that the pore-filled membrane did not show any increase in methanol permeation flux at an elevated temperatures of 130°C or higher, and kept its ability to highly inhibit methanol permeation up to about 180°C. On the other hand, a conventional electrolyte membrane, Nafion™ began to creep at about 130°C, and it no longer had its original form when the test completed.

From the description above, it will be appreciated that an electrolyte membrane can be provided which has a reduced methanol flux, heat-resistance at temperatures of 130°C or higher and improved proton conductivity which are required for an electrolyte membrane for DMFC.